

ORGANIC CONTAMINANTS IN SEDIMENTS FROM THE TRENTON CHANNEL OF THE DETROIT RIVER, MICHIGAN

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ABSTRACT. Anthropogenic organic contaminants in sediments from the Trenton Channel of the Detroit River, a highly industrialized waterway connecting Lake St. Clair with Lake Erie, were identified and quantified. The four major classes of organic contaminants identified were polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), polychlorinated naphthalenes (PCN), and polychlorinated terphenyls (PCT). Distributions of total PAH, the homologues of PCB and PCN, and total PCT were measured in 33 sediment samples. Concentration range maps revealed one region of relatively low contaminant concentration (southwest shore of Grosse Ile) and one area of high contaminant concentration in the vicinity of Monguagon Creek, located on the northwestern side of the Trenton Channel. Closer examination of total compound class and homologue concentration distributions suggests a hierarchical ordering of contaminant distribution similarity. Total PCT and PCN concentration distributions are most similar to one another, suggesting a common source in the vicinity of the Monguagon Creek mouth. PAH and PCB distributions are less similar to each other and to total PCT and PCN distributions, suggesting different sources of these compound classes.

ADDITIONAL INDEX WORDS: Toxic substances, chemical analysis, polychlorinated biphenyls, water pollution sources.

INTRODUCTION

The Detroit River, a strait which connects Lake St. Clair to the western basin of Lake Erie, is one of four major channels joining the Great Lakes. The river is 51 km long and drops about 1 m along its length. The flow is primarily southerly, with an average discharge rate of 5,200 m³/sec (Vaughn and Harlow 1965).

The lower portion of the Detroit River is a low-energy environment with flows varying from 0.15 to 0.60 m/sec and with significant deposition of fine-grained sediment (< 1 μ m mean particle diameter). This portion of the river has an average width of 2,000 m and an average depth of 7 m. Several islands located in this region divide the river into a system of channels, many of which are used as shipping lanes. One of these channels is the Trenton Channel (see Fig. 1) which runs between Grosse Ile and the U.S. mainland.

The Trenton Channel is a major depositional zone within the Detroit River; it is 0.25 to 1.2 km wide and is partly dredged to maintain a depth of 7 to 9 m. A small portion along the southern edge of the channel is not dredged and is only 3 m deep. Several chemical manufacturers discharge waste water containing significant amounts of complex hydrophobic organic compounds into the Trenton Channel. These compounds can concentrate on sediments and in biota. For example, Thornley and Hamdy (1984) and Hamdy and Post (1985) identified PCB (1,580 ng/g), DDT and its metabolites (186 ng/g), chlordane, and hexachlorobenzene in Trenton Channel sediments.

This paper addresses the following questions: (a) What are the distributions of well characterized organic contaminants (for example, PAH and PCB) endemic to the Trenton Channel of the Detroit River, and can these contaminants be related to specific sources? (b) Do Trenton Channel sediments contain any unusual organic contaminants, the distributions and environmental fates

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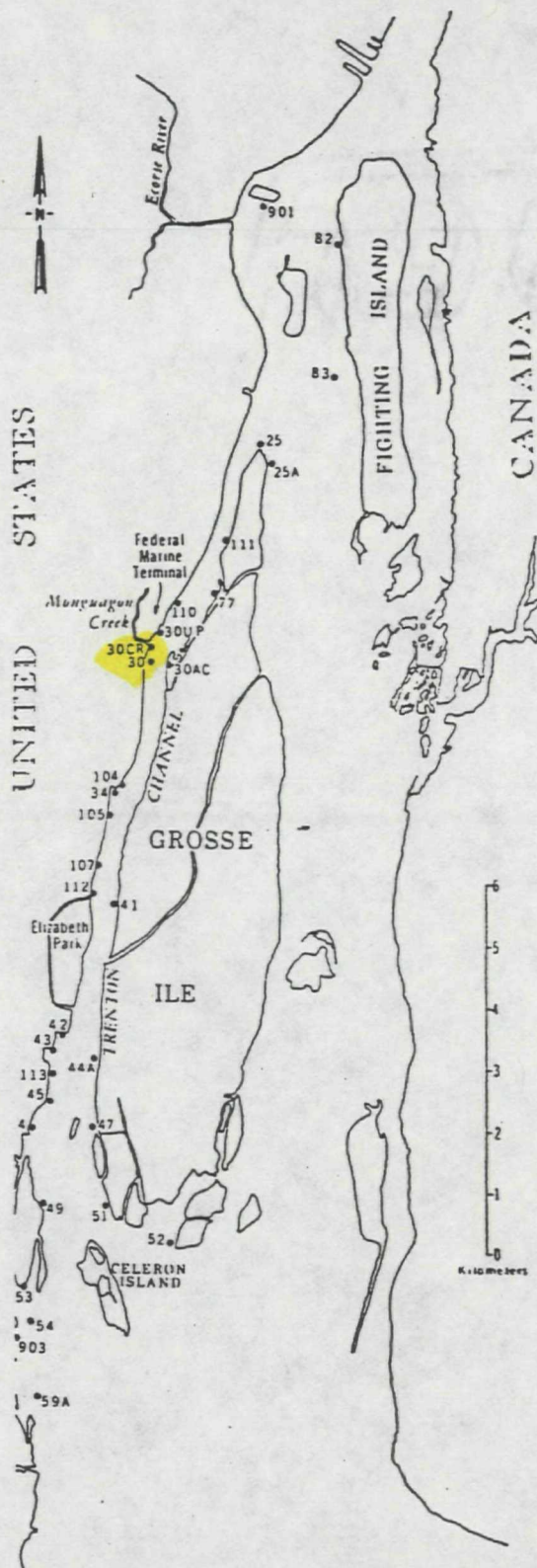


FIG. 1. Station numbers and locations for the sediment samples in the Trenton Channel of the Detroit River.

of which have not been previously assessed? What is their significance, and what are the sources for these compounds?

EXPERIMENTAL METHODS

Sampling

Sediments were collected in June through September of 1986 and June of 1987 by the U.S.E.P.A. Large Lakes Research Station at the stations indicated in Figure 1. Sediment grab samples were collected with a Ponar sampler, a representative aliquot (about 800 mL) was transferred to a solvent cleaned glass jar, and the jar was stored at 4°C. Samples were returned to the laboratory by common carrier, and stored at 4°C until extraction.

Extraction and Fractionation

Samples were homogenized by stirring the entire sample, and 15 to 20 g were removed for percent water determination. Another aliquot (10 to 30 g) was mixed with 30 to 70 g clean, anhydrous sodium sulfate to absorb sediment pore water; the resulting mixture had a loose, porous texture suitable for efficient extraction. Just prior to extraction, samples were spiked with two internal standards: a PCB (congener 204; 2,2',3,4,4',5,6,6'-octachlorobiphenyl) and an eight component perdeuterated polycyclic aromatic hydrocarbon (PAH) mixture. Each sample was extracted in a Soxhlet apparatus for 24 hours with isopropanol, followed by methylene chloride for an additional 24 hours. Sample volumes were reduced by rotary evaporation, combined, and solvent-exchanged to hexane.

Combined, hexane-exchanged extracts were chromatographed on columns containing 20 grams of 1% deactivated silica-gel, with HCl-rinsed copper at the bottom to adsorb elemental sulfur and a sodium sulfate "cap" at the top to absorb residual water. Samples were charged to the column in 3 mL of hexane and eluted sequentially with 45 mL of hexane, 45 mL of 10% methylene chloride in hexane, 45 mL of methylene chloride, and 45 mL of methanol. All fractions were collected separately. Fraction volumes were reduced by rotary evaporation, transferred to amber vials, and refrigerated.

Methylene chloride fractions from some sediment extracts (Station 30CR, for example) were not sufficiently separated from methanol fraction components due to high contaminant concentrations. These samples required a second fractiona-

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tion before analysis and were rechromatographed on a second silica column using an identical solvent elution scheme.

Analysis

All components except PAH were identified and quantitated using electron capture, negative ionization (ECNI) gas chromatographic mass spectrometry (GC/MS) using a Hewlett-Packard 5985B system equipped with a 30 m \times 0.25 mm, DB-5, fused silica capillary column. Helium was used as the carrier gas. Methane reagent gas was introduced into the ion source by a modified transfer line and regulated to an ion source pressure of 0.4 torr. The ion source temperature was held at 100°C. A GC temperature program, identical to that used for GC screening, was used to maximize compound separation (initial temperature 30°C, held for 3 minutes, temperature increased at 10°C/min to 100°C then at 4°C/min to a final temperature of 280°C, which was held for 50 minutes). A range of 50 to 750 daltons was scanned every 1.4 seconds. The emission current was approximately 200 μ A, and the electron energy was approximately 200 eV. Confirmation of compound identity was based on inspection of mass spectra and similarity of GC retention times when compared with standard Aroclors and Halowaxes.

Quantitation of halogenated aromatics was performed by generating mass chromatograms of selected ions from ECNI GC/MS total ion chromatograms. Mass chromatogram peak areas were electronically integrated, and compound amounts were calculated from response factors calculated for the compound in question relative to PCB congener 204, the internal standard. All halogenated aromatic compound classes were quantified by chlorine homologues. For example, there are 10 possible classes of PCB quantified in this study, corresponding to the number of possible chlorine substituents on the biphenyl skeleton.

Total ion chromatograms of commercial polychlorinated terphenyl (PCT) mixtures and sediment extracts are characterized by a poorly resolved series of broad peaks eluting at the end of a chromatogram. In this study, PCT was quantified by summing the ion abundances of the most common PCT ions (corresponding to Cl-9 to Cl-14 homologues) and quantifying with respect to PCB congener 204, using a response factor determined

for Aroclor 5460. This mixture contained the broadest range of PCT congeners and homologues in the commercially available Aroclors and appeared to be representative of sedimentary PCT. PCT concentrations are reported only as total PCT.

Polycyclic aromatic hydrocarbons (PAH) were identified and quantified on a Hewlett-Packard 5995 GC/MS system operated in the electron impact mode and equipped with a 25 m \times 0.25 mm, SE-54, fused silica capillary column. Helium was used as the carrier gas, and temperature programming (initial temperature 30°C, held for 4 minutes, temperature increased at 10°C/min to 160°C, then at 3°C/min to 290°C, which was held for 34 minutes) was used to achieve maximum PAH component separation. The electron energy was approximately 70 eV.

A selected ion monitoring (SIM) program similar to that used by McVeety (1986) was used for PAH quantitation. Molecular ions of the different PAH and their perdeuterated analogues were measured at the appropriate GC retention times. Selected ion chromatograms were generated and peak areas electronically integrated. Mixtures of PAH and deuterated PAH (from 50:1 to 1:50) were analyzed in the same manner as samples. From these standard analyses, calibration curves were developed and used to calculate PAH concentrations for any ratio of PAH to deuterio-PAH. Observed ratios of PAH to deuterio-PAH varied from approximately 10:1 to 1:3.

Sediment dry weights were calculated from percent water determinations. All concentrations are expressed in nanograms of compound per gram dry weight of sediment. Procedural blanks were taken through all phases of extraction, isolation, and analysis; final results were corrected for blank contributions, which were always very small.

Quality Control

Analytical reproducibility was assessed by triplicate subsample analyses of sediments with high and low contaminant concentrations (Stations 30CR and 25A, respectively). Quantitation precision of PCN, as individual homologues, ranged from 1.4 to 26% relative standard deviation (RSD). The precision for the PCB homologues ranged from 3 to 25% RSD. No systematic difference between high and low concentration samples was noted for any of the compound classes. Total

polychlorinated terphenyl (PCT) was at the detection limit in the low concentration samples. In high concentration samples, precision was 21% RSD.

The PAH method was independently checked for precision and accuracy by triplicate analysis of a National Bureau of Standards (NBS) reference material (SRM 1649). We reproduced NBS certified values, as expected from previous applications of the perdeuterated PAH internal standard technique to this SRM (McVeety 1986, Furlong *et al.* 1987, Roll 1986, Behymer and Hites 1985). PAH were quantified at the 100 picogram level using this technique.

RESULTS AND DISCUSSION

Thirty-three sediment samples were extracted, fractionated, and analyzed by GC and GC/MS (see Fig. 1). Examination of column chromatographic fractions indicated that chlorinated aromatic compounds eluted in the first two of the four fractions (these first two fractions were subsequently combined prior to GC/MS analysis) and polycyclic aromatic hydrocarbons eluted in the third. However, on a gravimetric basis, better than 50% of the Soxhlet extractable material is contained in the fourth (methanol) fraction, suggesting that this fraction, which is composed of a wide range of compounds typically classified as "polar," is likely to contain unique compounds which are not normally quantified in typical sediment extraction methods.

Quantitative results for PAH and PCB, as well as for the two relatively unknown compound classes, the PCN and PCT, are discussed below. These four compound classes, with some minor contributions from pesticides, octachlorostyrene, and penta- and hexachlorobenzene, were the major anthropogenic compounds eluting in the first three chromatographic fractions of Trenton Channel extracts.

Polycyclic Aromatic Hydrocarbons

Concentrations for 15 individual sedimentary PAH and their sum are given in Table 1. Individual PAH concentrations vary from not detected (<4 ng/g) to 22,000 ng/g. Individual and summed PAH concentrations were compared for all stations using a correlation matrix. There is an extremely high correlation between all individual PAH and summed PAH (arithmetic mean $r = 0.869 \pm 0.098$). This

suggests that the relative amount of each PAH are similar across a wide range of absolute concentrations. It also suggests that there is either a single PAH source, multiple sources which are not significantly different from one another, or that the PAH are well mixed prior to sedimentary deposition.

In addition to being compositionally uniform, the presence of significant quantities of photo-reactive PAH (such as anthracene and benzo[a]anthracene) in Trenton Channel sediments suggests that a PAH source other than combustion-derived atmospheric particulates contributes to the observed PAH signal. In sediments and atmospheric particulates collected at remote sites, where adsorbed PAH would have had significant exposure to sunlight, phenanthrene/anthracene and benzo[e]pyrene/benzo[a]pyrene ratios are about 16 and 2, respectively (McVeety 1986, Furlong *et al.* 1987), which reflect the relatively short photolytic half-lives of benzo[a]pyrene and anthracene (Behymer and Hites 1985). In contrast, Trenton Channel sediment ratios are 2.9 for phenanthrene/anthracene and 0.93 for benzo[e]pyrene/benzo[a]pyrene.

Total PAH concentrations measured in this study compare reasonably well with concentrations calculated from the data of Fallon and Horvath (1983, 1985) for six stations in their Trenton Channel study area. Due to the dynamic nature of the Trenton Channel sediment environment, large concentration differences are observed over short distances in both data sets (see Fig. 2); thus our 1986 results are not directly comparable to their 1982 results on a point-to-point basis. Furthermore, Fallon and Horvath made their measurements on homogenized 50-cm cores; thus, their concentrations would be expected to be lower than our surficial sediment samples.

Total PAH concentrations are highest (60,000 to 130,000 ng/g) at Stations 30CR, 110, and 112 (see Table 1 and Fig. 2). Stations 30CR and 110 are located just downstream of the Wyandotte Chemical Co. in the vicinity of the Federal Marine Terminal, a hazardous waste disposal site. Station 112 is adjacent to a Mobile Oil refinery site near Elizabeth Park. These are potentially significant sources of PAH to the immediate vicinity. However, locally high PAH concentrations at sites more distant from suspected point sources are less easily explained. Deposition of PAH rich, fine-grained particles in certain regions of the Trenton Channel is likely to be a major complicating factor.

TABLE 1. Individual and summed polycyclic aromatic hydrocarbon concentrations (ng/g dry weight of sediment) in Trenton Channel sediments.

Station	Acenaph-thene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz(a)anthracene	Chrysene	Benzofluoranthenes	Benzo(e)pyrene	Benzo(a)pyrene	Perylene	Benzo(ghi)Perylene	Coronene	Summed PAH
25A	220	330	1,500	730	2,300	2,200	1,100	1,700	2,100	880	1,500	410	890	230	16,000
25	530	1,400	2,800	2,200	4,500	4,400	2,000	2,800	3,800	1,600	2,800	670	1,500	360	31,000
30	380	810	3,500	1,500	5,400	4,900	3,700	3,300	5,700	2,100	3,700	910	2,000	750	39,000
30AC	84	160	810	330	1,500	1,300	660	1,100	1,800	710	1,100	320	640	190	11,000
30CR	370	880	5,500	2,600	1,400	11,000	5,400	8,900	12,000	4,700	7,400	2,100	5,000	1,200	81,000
30UP	270	560	2,300	820	3,800	3,400	2,700	2,400	3,500	1,400	2,400	760	1,600	670	27,000
34	160	380	1,600	540	3,100	2,900	1,400	2,400	3,500	1,500	2,400	740	66	410	21,000
41	240	510	2,300	1,100	4,000	3,500	1,900	2,800	3,700	1,600	2,800	780	1,600	390	27,000
42	340	720	2,900	950	4,300	4,200	2,200	3,800	4,700	2,500	3,400	1,000	2,500	640	34,000
43	1,100	330	1,500	350	2,800	3,100	2,300	2,300	2,900	1,500	2,000	540	1,200	440	22,000
44A	130	230	1,600	660	3,900	3,300	1,600	2,600	3,800	1,500	2,500	650	1,500	330	24,000
45	150	290	1,600	490	3,200	2,900	1,400	2,700	3,800	1,800	2,500	670	1,600	420	24,000
47	140	280	1,200	700	2,700	2,600	2,100	2,000	2,400	1,000	2,000	520	970	440	19,000
49	130	210	1,200	400	2,000	1,700	910	1,400	1,900	990	160	330	860	180	12,000
51	10	22	120	37	210	210	120	130	340	81	120	36	72	32	1,400
52	n.d.	n.d.	50	8.8	38	38	17	52	57	26	33	4.0	27	n.d.	350
53	58	170	690	240	1,400	1,700	1,300	1,600	2,300	1,100	1,500	480	1,100	260	14,000
54	180	290	1,500	620	2,700	2,500	2,200	2,100	3,400	1,400	2,600	720	1,500	510	22,000
59A	60	170	880	350	1,500	1,400	1,600	1,500	2,800	1,100	1,800	470	1,000	230	15,000
77	260	530	2,300	890	4,000	3,800	2,900	2,800	4,900	1,900	3,800	970	1,600	660	31,000
82	n.d.	7.7	64	20	120	120	100	78	170	74	74	n.d.	54	15	890
83	n.d.	n.d.	100	41	200	160	69	110	180	73	110	41	66	n.d.	1,200
104	200	380	1,500	460	2,000	1,700	1,400	1,200	2,600	960	1,600	450	990	300	16,000
105	250	470	2,100	650	20,000	2,800	1,600	2,400	3,500	1,800	2,100	730	1,700	370	41,000
107	520	1,500	5,341	1,600	6,000	5,400	2,500	4,500	5,400	2,500	3,700	1,200	2,400	650	43,000
110	920	1,800	15,000	3,300	22,000	20,000	9,200	12,000	16,000	7,900	9,900	3,000	7,600	1,600	130,000
111	470	760	4,500	1,600	5,100	4,500	2,600	4,200	6,000	3,100	4,400	1,400	4,100	1,200	44,000
112	520	1,200	5,300	2,000	7,100	7,000	3,700	6,900	8,900	4,200	6,100	1,700	3,900	950	60,000
113	46	75	430	140	960	940	470	870	1,200	570	820	210	500	92	7,300
114	45	120	560	140	1,100	1,000	440	910	1,200	630	670	200	480	120	7,700
901	480	560	2,600	1,700	5,200	4,300	4,200	3,600	5,300	2,100	3,900	1,100	1,800	780	38,000
902	58	150	630	170	1,600	1,900	1,000	1,300	2,100	920	1,000	360	810	360	12,000
903	n.d.	49	340	50	490	330	160	220	380	160	140	n.d.	130	69	2,500

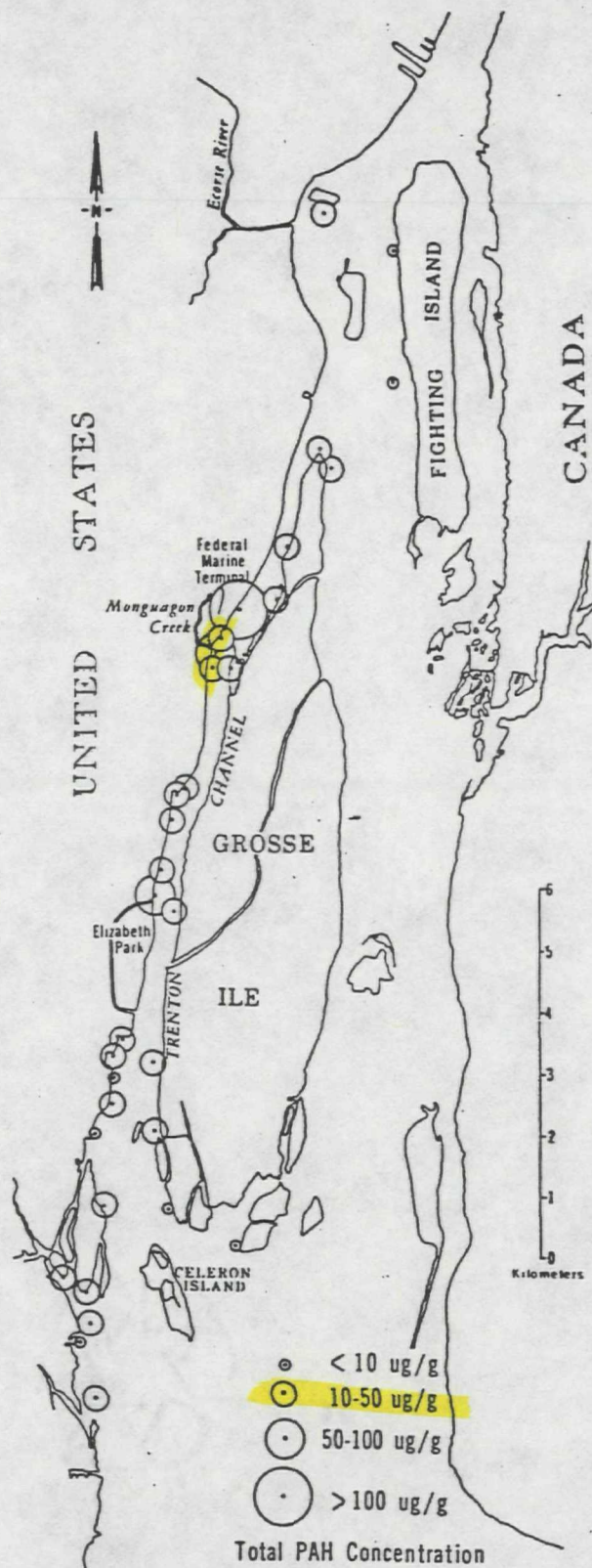


FIG. 2. Total polycyclic aromatic hydrocarbon concentrations (ng/g dry weight) in Trenton Channel sediments; see last column of Table 1.

PAH concentrations throughout the Trenton Channel are indicative of significantly contaminated sediments. Sediment samples from remote sites typically contain total PAH concentrations under 10,000 ng/g (Furlong *et al.* 1987, McVeety 1986; Heit *et al.* 1981) in comparison to total PAH concentrations of up to 130,000 ng/g in Trenton Channel sediments. This is particularly remarkable given that the likely residence time of Trenton Channel surface sediments is short, suggesting that the yearly throughput of PAH is high. The Detroit River-Trenton Channel could be a significant PAH source to Lake Erie, both in the western region and lakewide, depending on the dynamics of lake sediment transport.

Polychlorinated Biphenyls

PCBs are well recognized environmental contaminants; they have been identified in sediments, water, air, and biota from both pristine and highly polluted environments (Oliver, 1985, Erickson 1986, Brownawell and Farrington 1986, Kimbrough 1980, Brown *et al.* 1987). Previous investigations of Detroit River sediments have indicated PCB contamination ranging up to 3,800 ppb (Hamdy and Post 1985, Kaiser *et al.* 1985).

The total PCB concentrations (sum of Cl_2 to Cl_{10} homologues) measured in this study are illustrated in Figure 3. Table 2 gives the total PCB and individual chlorine homologue concentrations for these samples. The highest PCB concentrations occur at Stations 77 and 107 with significantly lower levels both upstream and downstream of these stations (see Fig. 3). The observed distribution is similar to that of total PAH (see Fig. 2), and it can arise from two processes: (a) input from upstream and within-channel sources, and (b) fine-grained, PCB-enriched sediments concentrating in deposition zones. Significant sedimentary PCB contamination both upstream and downstream of the Trenton Channel has been observed previously (Oliver and Bourbonniere 1985, Kaiser *et al.* 1985); this suggests that multiple sources of PCB are contributing to the sediment transported through the Trenton Channel. Thus, Trenton Channel sediment PCB contamination is not necessarily from within channel sources, rather it originates from pre-contaminated sediment transport.

Concentrations and distributions of PCB chlorine homologues provide some additional information. In the United States, commercial PCB mixtures were distributed primarily as 1200 series

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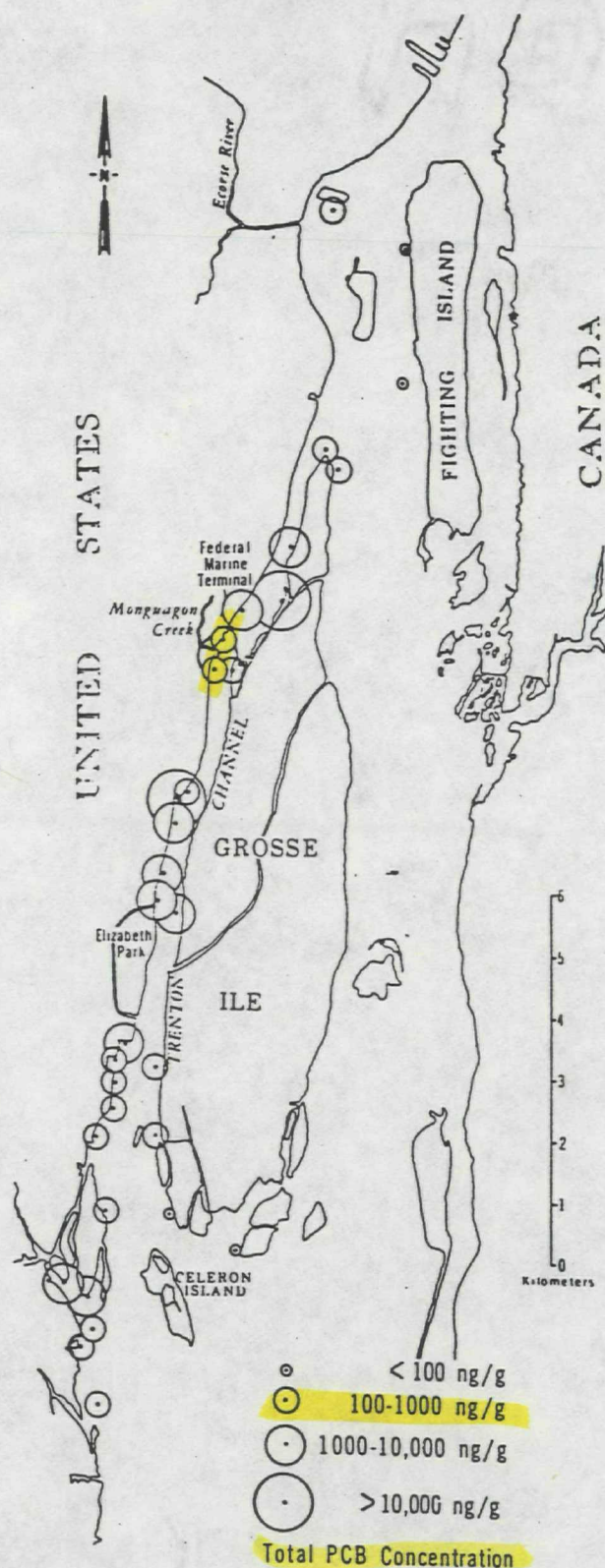


FIG. 3. Total polychlorobiphenyl concentrations (ng/g dry weight) in Trenton Channel sediments; see last column of Table 2.

Aroclor mixtures by the Monsanto Company; these mixtures had relatively well-defined percentages of chloro-homologues in each (Hutzinger *et al.* 1974, Brinkman and de Kok 1980). Many previous analytical methods for PCB have attempted to quantify environmental PCB contamination in terms of the concentration of an Aroclor mixture (Erickson 1986). However, observed homologue distributions can reflect differential degrees of solubility, sediment adsorption, vaporization, and bioaccumulation (Pearson, 1982).

Relative to commercial PCB mixtures, the chlorine homologue compositions observed in Trenton Channel sediments are skewed toward higher chlorine homologues (Cl_8 to Cl_{10} PCB), as would be expected from lower homologue volatility, adsorption, and solubility (Hutzinger *et al.* 1974). Large concentrations of decachlorobiphenyl may result from direct inputs of this homologue which was commercially produced and imported into the United States in significant quantities (Brinkman and de Kok 1980). The higher PCB homologues are also contained in PCT mixtures (Aroclor 5400 series; Brinkman and de Kok 1980). When compared to Aroclor homologue compositions, di-through nona-chloro PCB homologue distributions in Trenton Channel sediments are significantly altered from what would be expected from unaltered commercial Aroclors (Hutzinger *et al.* 1974).

In contrast with our observations, a recent report (Brown *et al.* 1987) has suggested that reductive dechlorination of higher chlorination PCB homologues occurs within anoxic Hudson River sediments located downstream from a major PCB source. Although the degree of sediment anoxia was not determined in this study, many of the samples, particularly the most fine-grained sediments, are likely to be reducing. Other authors (Brownawell and Farrington 1986) observed an enrichment of higher chlorinated PCB homologues in sediments from New Bedford Harbor, a severely PCB-contaminated environment. They attributed the observed PCB distributions to partitioning between sediments, water, and dissolved organic colloids. Grab samples were collected in our study, so depth profiles of PCB homologue distributions cannot be determined; it would be an important priority in future studies to determine if reductive dechlorination or porewater transport is a significant process altering observed, Trenton Channel, PCB homologue distributions.

TABLE 2. Individual homologue and summed polychlorobiphenyl (PCB) concentrations (ng/g dry weight of sediment) in Trenton Channel sediments.

Station	Cl-3 PCB	Cl-4 PCB	Cl-5 PCB	Cl-6 PCB	Cl-7 PCB	Cl-8 PCB	Cl-9 PCB	Cl-10 PCB	Total PCB
25A	n.d.	100	210	330	260	44	8.4	1.3	950
25	n.d.	77	120	160	120	15	3.4	0.7	500
30	n.d.	n.d.	n.d.	4.1	31	28	37	50	150
30AC	n.d.	63	98	190	150	20	5.3	0.9	520
30CR	n.d.	480	340	950	1,200	220	39	11	3,300
30UP	n.d.	n.d.	24	76	110	55	45	81	390
34	59	720	830	830	490	87	16	11	3,100
41	n.d.	220	260	300	210	33	23	12	1,100
42	94	560	890	960	610	140	36	52	3,300
43	n.d.	66	180	200	130	36	11	6.8	630
44A	16	150	120	79	41	8.5	4.7	1.0	420
45	n.d.	110	140	180	130	22	10	8.2	600
47	n.d.	67	68	60	43	8.1	3.9	1.4	250
49	81	110	190	220	150	25	6.7	5.7	780
51	n.d.	2.5	2.1	6.9	10	1.5	1.4	0.4	25
52	n.d.	2.1	3.4	3.1	0.8	n.d.	0.014	0.1	9.5
53	145	250	350	410	330	65	14	6.5	1,600
54	n.d.	33	51	75	64	25	16	14	280
59A	n.d.	75	140	150	98	28	13	6.8	510
77	297	1,300	2,200	3,800	4,000	1,300	270	50	13,000
82	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
83	n.d.	3.9	5.6	3.6	0.5	0.2	n.d.	0.4	14
104	n.d.	63	150	140	72	9.5	4.4	3.3	440
105	322	1,300	1,300	770	350	76	20	18	4,100
107	1,352	5,100	4,500	2,100	720	150	45	120	14,000
110	n.d.	520	2,900	2,000	1,000	430	140	140	7,200
111	46	240	280	310	220	39	12	6.7	1,100
112	259	1,100	1,300	1,400	860	190	38	18	5,100
113	n.d.	120	170	150	70	10	0.8	1.4	510
114	n.d.	160	230	250	140	20	3.1	4.0	790
901	n.d.	100	130	200	140	25	4.3	0.9	610
902	n.d.	180	300	500	420	94	25	12	1,500
903	n.d.	51	66	65	34	2.0	0.9	0.9	220

Polychlorinated Naphthalenes

Polychlorinated naphthalenes (PCN) have been commercially produced since World War I. They have physical and chemical properties similar to PCB, but since the introduction of PCB in 1929, PCN have comprised a much smaller fraction of commercial haloaromatic compound production (about 10% of PCB production; Brinkman and de Kok 1980). Commercial uses of PCN prior to the 1950s were as dielectrics, water repellants, and lubricants. After the 1950s, production declined, and since 1973, the major use has been in automobile capacitors (Brinkman and Reymer 1976).

Environmental PCN concentrations have not

been extensively reported (Kimbrough 1980, Jaffe and Hites 1984). PCN have been noted in Detroit River samples, but not previously reported or quantified (M. Mullin, personal communication). Trenton Channel total PCN concentrations are mapped in Figure 4, and total PCN and individual chlorohomologue concentrations are listed in Table 3.

By far the highest PCN concentration (61,000 ng/g) is found at site 110; stations just downstream of this site also show high PCN concentrations. Since PCN concentrations had not been reported in other Detroit River studies, it was not clear whether PCN contamination was systemic in the

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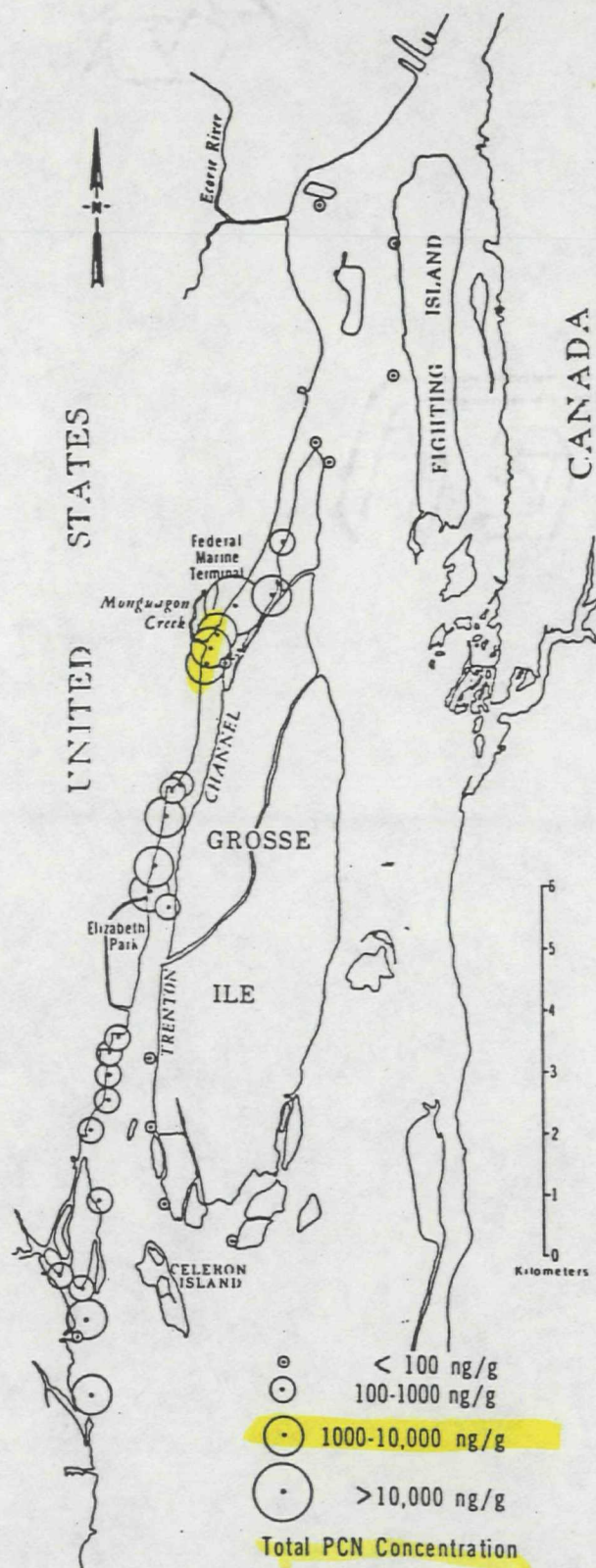


FIG. 4. Total polychloronaphthalene concentrations (ng/g dry weight) in Trenton Channel sediments; see next to the last column of Table 3.

Detroit River or localized in the Trenton Channel. Our measurements of five samples north of both Station 110 and the channel proper (Stations 901, 82, 83, 25, and 25a) show negligible (0 to 10 ng/g) PCN concentrations, suggesting that there are few upstream PCN sources. It is especially important to note that Stations 901 and 85 are primarily composed of fine-grained accretionary sediment, which would have adsorbed PCN during transport, if they had been introduced in significant concentrations upriver.

Compositional alteration of sedimentary PCN chlorine homologue distributions is expected to be affected by processes similar to those altering PCB. However, homologue compositions of commercial PCN mixtures (Halowax 1000 series) are less well-known than those of PCB. Significant octachloronaphthalene concentrations were measured, and octachloronaphthalene is the major component of the commercial mixture, Halowax 1051. However, the extent of its production by the two major U.S. manufacturers of PCN mixtures, The Koppers Co. (until 1977; Brinkman and de Kok 1980) and Halochem (which produces an equivalent mixture, N-wax 80) is not known. Total U.S. production of all PCN mixtures in 1978 was estimated to be 700,000 lbs. (Brinkman and de Kok 1980).

Due to similarity in physical and chemical properties (Hutzinger *et al.* 1974, Brinkman and Reymer 1976), PCB and PCN in Detroit River sediments co-eluted over a very similar time window. Examination of electron capture GC or total ion GC/MS chromatograms were insufficient to determine component identity. Sufficient resolution and quantitation of the co-eluting compound classes were achieved only by utilizing mass chromatograms of homologue specific PCB or PCN ions. Unless unequivocal chromatographic separation can be achieved, PCNs can be a significant contributor to estimated PCB concentrations.

Polychlorinated Terphenyls

Polychlorinated terphenyls (PCT) are chlorinated three ring analogues of PCB. PCT production was a small fraction of that of PCB (maximum U.S. production: 10^7 kg in 1971, Brinkman and de Kok 1980). PCT were commercially produced by Monsanto (Aroclor 5400 series) and marketed as PCT and as PCB-PCT mixtures. PCT have been identified and quantitated in fish, gull eggs and tissue, oysters, and human fat samples (Doguchi *et al.*

TABLE 3. Individual homologue and summed polychloronaphthalene (PCN) and total polychloroterphenyl (PCT) concentrations (ng/g dry weight of sediment) in Trenton Channel sediments.

Station	Cl-2 PCN	Cl-3 PCN	Cl-4 PCN	Cl-5 PCN	Cl-6 PCN	Cl-7 PCN	Cl-8 PCN	Total PCN	Total PCT
25A	n.d.	2.1	2.7	0.43	1.5	1.4	0.41	8.5	1.4
25	n.d.	0.64	1.7	0.49	0.76	0.56	0.24	4.4	1.2
30	2.4	400	520	710	880	710	100	3,300	2.1
30AC	n.d.	23	30	16	18	9.0	2.0	97	21
30CR	n.d.	120	270	150	280	180	13	1,000	350
30UP	n.d.	130	230	390	440	370	52	1,600	31
34	0.1	150	220	140	150	98	13	770	84
41	n.d.	72	82	35	31	16	1.8	240	15
42	0.63	170	240	110	160	140	20	840	260
43	0.40	140	210	120	150	120	12	750	3.5
44A	n.d.	15	25	14	7.6	4.8	1.1	68	26
47	n.d.	16	25	15	14	7.6	1.0	80	1.7
49	0.22	53	100	79	98	69	8.9	410	180
51	n.d.	1.0	1.9	2.1	1.9	1.4	0.18	8.5	1.3
52	n.d.	0.12	0.22	0.033	0.014	0.026	n.d.	0.41	n.d.
53	n.d.	52	110	64	64	41	5.2	330	170
54	0.48	160	270	350	380	410	56	1,600	320
59A	n.d.	130	240	200	270	290	42	1,100	240
77	n.d.	230	640	510	820	630	55	2,900	350
82	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
83	n.d.	0.31	0.49	n.d.	0.15	0.20	n.d.	1.1	n.d.
104	n.d.	160	160	87	89	75	11	580	490
105	1.1	230	320	260	240	170	18	1,200	210
107	1.5	510	670	470	430	300	31	2,400	400
110	10	7,800	21,000	15,000	11,000	5,700	420	61,000	2,500
111	0.14	61	110	230	370	170	13	950	260
112	1.7	440	800	710	730	570	59	3,300	720
113	n.d.	94	180	160	130	75	7.0	640	17
114	n.d.	93	130	56	64	50	2.3	400	0.67
901	n.d.	0.75	1.8	0.45	2.6	n.d.	n.d.	5.7	0.063
902	n.d.	22	61	67	83	57	5.0	300	120
903	n.d.	21	36	12	8.5	4.4	0.39	83	34

1974, Freudenthal and Greve 1973, Zitko *et al.* 1972, Jan and Malnersic 1978), as well as in Rhine River water (Freudenthal and Greve 1973). Documented PCT contamination of sediments and soils has ranged from <0.2 ppm to 13 ppm, near a potential source (Stratton and Sosebee 1975).

PCT are compositionally complex and contain both chlorine positional isomers and positional isomers of the third phenyl ring (ortho, meta, and para). In addition, commercial PCT mixtures have a significant (about 1% by wt) PCB component. Our examination of 5400 series Aroclors indicated PCB homologue distributions ranged primarily from Cl₅ to Cl₁₀ biphenyls.

Total PCT distributions are mapped in Figure 5

and listed in Table 3. PCT concentrations range over three orders of magnitude, from a high of 2,500 ng/g at Station 110 to undetectable concentrations both upstream and downstream of the central Trenton Channel. Previous reports of environmental PCT contamination have linked them with investment casting facilities (Stratton and Sosebee 1975). Although U.S. production of PCT ceased in 1971, PCT have been imported primarily for use as slow shrinkage wax fillers in investment casting (Brinkman and de Kok 1980). This use, coupled with the absence of quantifiable PCT concentrations upstream of the Trenton Channel, and slowly decreasing concentrations downstream, suggests a localized PCT source associated with

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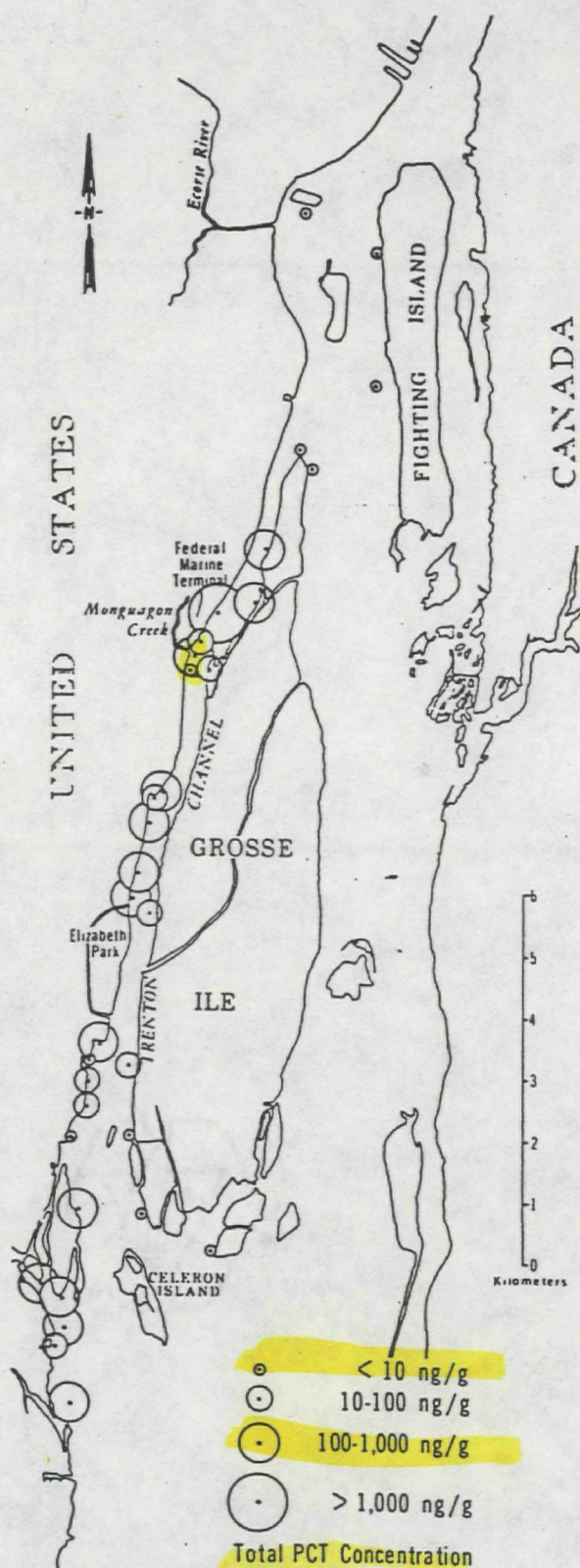


FIG. 5. Total polychloroterphenyl concentrations (ng/g dry weight) in Trenton Channel sediments; see last column of Table 3.

one or more of the industrial concerns currently or formerly operating in the vicinity of Station 110. This site is adjacent to a closed steel products factory. However, other commercial concerns, as well as a hazardous waste site (the Federal Marine Terminal), are located in this region; thus, final linkage of PCT to a specific point source is tentative.

Transport and Behavior of Organic Contaminants in Trenton Channel Sediments

Two distinct contaminant distributions are reflected in the concentration range maps given in Figures 2 through 5. Total PAH and PCB concentration distributions are elevated in stations upstream of the Trenton Channel, suggesting upstream sources of these compounds. In contrast, total PCN concentrations increase from below the detection limit to 8.5 ng/g upstream to 1,000 to 61,000 ng/g in the vicinity of Stations 30CR, 77, and 110. Similarly, total PCT concentrations increase from 0 to 1.4 ng/g upstream to 350 to 2,500 ng/g at the same three stations. For most samples, sediment concentrations of all four compound classes are elevated downstream from those three stations. Highest concentrations of PCN, PCT, and PAH occur at Station 10. PCB concentrations are highest upstream and downstream of Station 110, at Stations 77 and 107.

A correlation matrix was generated comparing the totals of all four organic compound class distributions with each other. The data were paired on a site-by-site basis. An analogous matrix was generated to produce Spearman rank-ordered correlation coefficients for the same organic compound classes. In both unranked and rank-ordered data sets, all four compound classes were significantly correlated. However, the correlation was higher between PCT and PCN than between PCB and PCN or between PCB and PCT. Results for correlations with PAH indicated higher correlation with PCN and PCT when the data were unranked. Rank ordered results were equivocal. Taken together, these statistical tests suggest a sequential order of correlation between compound distributions. PCN and PCT spatial distributions are most similar to each other. PAH distributions are somewhat similar to PCN and PCT, and PCB distributions are least similar to the other three compound classes.

These comparisons refer to only the summed (total) compound classes. In a correlation matrix for individual PCB-chlorine homologues, correla-

tion coefficients varied markedly with each other and with total PCN or PCT. Correlation coefficients ranged from not significant to highly significant. This is probably the result of multiple PCB sources. In comparison, PCN homologues are strongly correlated with each other and with total PCT, further suggesting that sediment PCN and PCT concentrations are derived from a single source for both compound classes.

Finally, spatial heterogeneity should be considered the characteristic most common to all compound distributions (see Figs. 2 through 5). Stations close to each other may have one or two orders of magnitude concentration differences for any single compound class. We also note two larger scale spatial features: (a) a region of relatively low PCN, PCB, PCT, and PAH concentrations along the southwest shore of Grosse Ile, and (b) elevated contaminant concentrations along the western shore of the Trenton Channel. The abundance of potential contaminant sources along the western shore of the Trenton Channel (Thornley and Hamdy 1984) may explain the observed high contaminant concentrations. However, the southwest shore of Grosse Ile is a depositional site for fine-grained sediments (Fallon and Horvath 1983, 1985), and hence it is a potential sink for contaminated sediments from upstream of this region. The complex interactions between contaminant sources, suspended sediment load, and in-channel sediments require further investigation before the heterogeneous distributions of sediment contaminant concentrations can be explained.

Other Potential Contaminant Tracers

Several cholesterol derivatives, primarily cholestanols, were identified in central Trenton Channel sediments at station 30CR. These compounds result from intestinal microbial reduction of unsaturated sterols during mammalian metabolism. Since cholestanols are not present to any appreciable extent in natural waters, these compounds are indicative of fecal contamination (Smith *et al.* 1968). Cholesterol levels in sewage drop drastically upon activated sludge treatment of the sewage (Smith *et al.* 1968); thus, cholestanol concentrations can be used to track deposition patterns of sediments contaminated with untreated sewage. However, cholestanols can only be used as an indicator for moderately short range transport studies because these contaminants have many localized sources.

Tertiary alkyl phenols were identified in sediments from station 30CR at the mouth of Monguagon Creek; 2,4-di-*tert*-pentylphenol was the most abundant alkyl phenol identified. Pennwalt Organic Chemicals Division, which produces these compounds, is located on the creek about 0.8 km upstream of the sampling site. The Pennwalt plant on Monguagon Creek is the sole producer of this compound in the Great Lakes area; thus, this compound seems to have a single point source. Initial results indicate that 2,4-di-*tert*-pentylphenol is not present in riverine sediment samples taken upstream of site 30CR and that it rapidly disappears downstream. Selected ion monitoring techniques are currently being developed to identify and quantify these phenols in Trenton Channel sediments.

SUMMARY

Analyses of Trenton Channel sediments indicate a wide range of contaminant loading to sediments. Station 110, near Monguagon Creek, is the most contaminated site. PAH, PCN, and PCT are most abundant at this site; there are low contaminant concentrations upstream of this site and decreasing contaminant concentrations downstream. In addition to the common PCB and PAH, two novel classes of haloaromatic compounds, the polychlorinated naphthalenes (PCN) and the polychlorinated terphenyls (PCT) were identified and quantified. PCN and PCT seem to come from a within-channel source, and these compounds could serve as a unique chemical indicator of sediment-transported organic contaminants from the Trenton Channel to Lake Erie.

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